

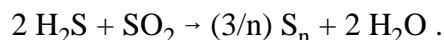
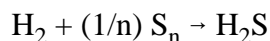
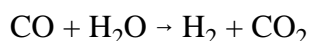
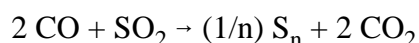
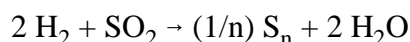
Bench-Scale Demonstration of Hot-Gas Desulfurization Technology

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Introduction

Designs for advanced integrated gasification combined cycle (IGCC) power systems call for desulfurization of coal gasifier gas at high-temperature, high-pressure (HTHP) conditions using highly efficient, regenerable metal oxides such as zinc titanate. Regeneration of the sulfided sorbent using an oxygen-containing gas stream results in a sulfur dioxide (SO₂)-containing off-gas at HTHP conditions. Over the past 10 years, the U.S. Department of Energy/Federal Energy Technology Center (DOE/FETC) has sponsored a number of approaches for ultimate disposal of this off-gas. The patented Direct Sulfur Recovery Process (DSRP) being developed by Research Triangle Institute (RTI) is a highly attractive option for recovery of sulfur from this regeneration off-gas. Using a slipstream of coal gas as a reducing agent, it efficiently converts the SO₂ to elemental sulfur, an essential industrial commodity that is easily stored and transported.

In the DSRP (Dorchak et al., 1991), the SO₂ tail gas is reacted with a slipstream of coal gas over a fixed bed of a selective catalyst to directly produce elemental sulfur at the HTHP conditions of the tail gas and coal gas. Overall reactions involved are shown below:



Slipstream tests with actual coal gas (Portzer and Gangwal, 1995; Portzer et al., 1996), demonstrated that, with careful control of the stoichiometric ratio of the gas input, sulfur recovery of 96 to 98 percent can be consistently achieved in a single DSRP stage. The single-stage process, integrated with a metal oxide sorbent regenerator, is shown in Figure 1. Since the tail gas from the DSRP can be recycled as shown in the figure, there are no sulfur emissions from the DSRP.

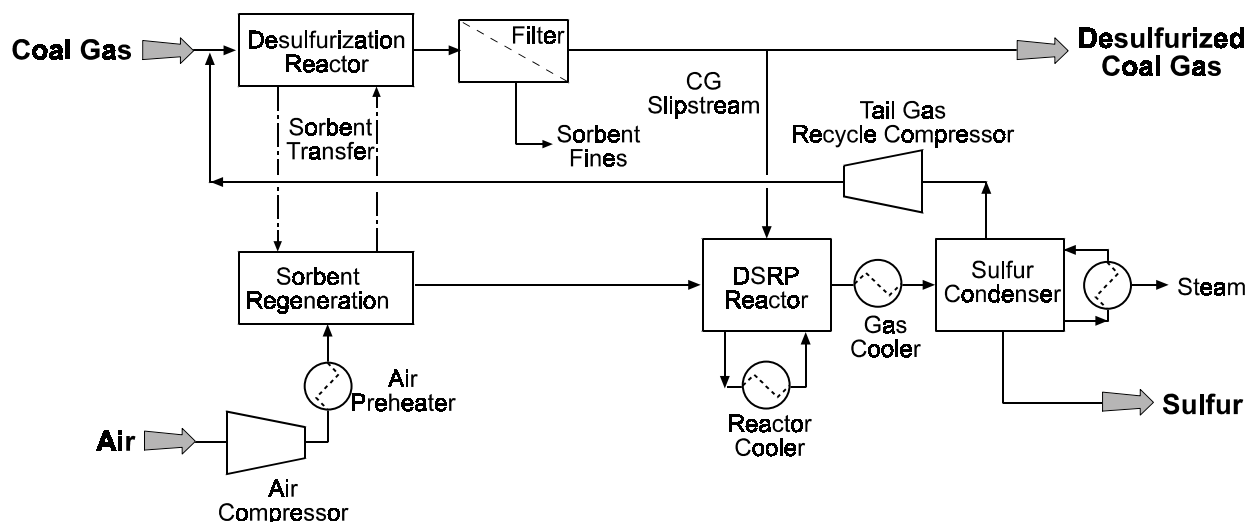


Figure 1. Hot-gas desulfurization with DSRP.

Objectives

Prior to the current project, development of the DSRP was done in a laboratory setting, using synthetic gas mixtures to simulate the regeneration off-gas and coal gas feeds. The objective of the current work is to further the development of zinc titanate fluidized-bed desulfurization (ZTFBD) and the DSRP for hot-gas cleanup by testing with actual coal gas. The objectives of this project are to:

- Develop and test an integrated, skid-mounted, bench-scale ZTFBD/DSRP reactor system with a slipstream of actual coal gas;
- Test the bench-scale DSRP over an extended period with a slipstream of actual coal gas to quantify the degradation in performance, if any, caused by the trace contaminants present in coal gas (including heavy metals, chlorides, fluorides, and ammonia);
- Expose the DSRP catalyst to actual coal gas for extended periods and then test its activity in a laboratory reactor to quantify the degradation in performance, if any, caused by static exposure to the trace contaminants in coal gas;
- Design and fabricate a six-fold larger-scale DSRP reactor system for future slipstream testing;
- Further develop the fluidized-bed DSRP to handle high concentrations (up to 14 percent) of SO_2 that are likely to be encountered when pure air is used for regeneration of desulfurization sorbents; and

- Conduct extended field testing of the 6X DSRP reactor with actual coal gas and high concentrations of SO₂.

The accomplishment of the first three objectives—testing the DSRP with actual coal gas, integration with hot-gas desulfurization, and catalyst exposure testing—was described previously (Portzer and Gangwal, 1994, 1995; Portzer et al., 1996). This paper summarizes the results of previous work and describes the current activities and plans to accomplish the remaining objectives.

Approach

Because coal gas is not available at RTI's laboratories in Research Triangle Park, North Carolina, other approaches were used to accomplish the desired DSRP testing. The first strategy—slipstream testing—moved the existing bench-scale DSRP apparatus to a coal gas source (the FETC 10-in. fluidized-bed gasifier at Morgantown) by housing it in a mobile laboratory. At Morgantown, the bench-scale process equipment was operated to produce elemental sulfur using a small slipstream of the total gasifier output.

The second strategy—canister testing—moved only the catalyst to the source of the coal gas (General Electric [GE] pilot-plant gasifier) and exposed it for an extended period. The exposure was followed by testing in a second bench-scale DSRP unit in the RTI laboratory that used simulated coal gas to verify the catalyst's continued efficacy following exposure.

Both strategies—slipstream testing and canister exposure testing—will be used in planned future activities as well.

Project Description

The equipment used for the Morgantown slipstream testing, RTI's ZTFBD/DSRP mobile laboratory (trailer), was previously described (Portzer and Gangwal, 1994). The DSRP was operated in conjunction with gasifier campaigns at Morgantown in 1994 and 1995. During the July 1995 campaign actual coal gas was flowing through the DSRP catalyst bed for more than 160 h. The simulated regeneration off-gas was fed to the catalyst bed for a total of 44 h, divided into nine separate periods of multihour operation.

The duration of the runs with SO₂ flowing was limited by problems associated with solid sulfur plugging of the downstream vent lines.

Several months following completion of the 160-h slipstream run, the DSRP catalyst was removed from the reactor, placed in a canister, and installed in a coal gas line at the GE pilot gasifier in Schenectady, New York. Table 1 shows the GE exposure test conditions. The idea of the canister exposure test was

Table 1. GE Exposure Test Conditions

<ul style="list-style-type: none"> • 20 atm (294 psia) • 482 to 538 °C (900 to 1,000 °F) • Illinois #6 Coal Gas • 200 h • Downstream of absorber

that the DSRP catalyst would have 200 h of additional exposure to actual coal gas (beyond what was achieved during the Morgantown Energy Technology Center [METC] 160-h campaign) so that the effect, if any, of the trace contaminants could be determined.

To determine if additional coal gas exposure of the catalyst had any deleterious effects, the doubly exposed catalyst was tested in a bench-scale DSRP unit set up in a laboratory in RTI's main campus in Research Triangle Park. The reactor design was essentially identical to that of the trailer-mounted unit; the sulfur condenser design was identical. The coal gas was simulated by using a purchased custom gas mixture, and the regeneration off-gas was generated similar to the method used in the trailer—vaporization of liquid SO₂ under pressure. Table 2 summarizes the operating conditions of the DSRP reactor in the Mobile Laboratory (1995 slipstream test) and compares them to the conditions used for the followup testing of the exposed catalyst (1996 testing) in the RTI laboratory. The conditions are very similar, except that less catalyst was available for the laboratory tests (due to a limitation of canister volume). However, the gas flow rate was reduced to maintain the same space velocity.

A major task on this contract has been the design and fabrication of a larger-scale DSRP apparatus for slipstream testing. A six-fold larger unit (based on fixed-bed reactor catalyst volume) has been designed and assembled on an easily transportable steel-framed skid at RTI; it is conveniently referred to as the “6X” unit. Table 3 summarizes some key design parameters of this new test unit; Figures 2 and 3 are photographs of the skid in the RTI fabrication shop. Because of its size, the equipment will not fit inside the mobile laboratory. The larger test unit is expected to yield improved engineering design data, scale-up data, and enhanced operability. Working with larger diameter lines and greater volumes of reactants, it is anticipated that unscheduled outages due to sulfur plugging will be minimized. Subsequent to the original design of the 6X unit, the test plan was changed to focus on fluidized-bed reactor designs. Thus, as Table 3 shows, the 6X unit is being redesigned as a fluidized-bed test unit and no longer has a nominal 6-fold larger catalyst capacity. However, with the capability to handle higher SO₂ in the feed, the sulfur production capacity is up to 22 times larger.

Table 2. Reactor Test Conditions

	1995 Field Test	1996 Lab Test
Temperature (°C)	590-630	575-640
Pressure, atm (psig)	15.3-19 (210-265)	19.7 (275)
Space velocity (std cm ³ /cm ³ -h)	5,100	2,700-8,200
Reactor diameter (cm [in.])	7.6 (3.0)	7.6 (3.0)
Catalyst volume (cm ³)	1,000	600
Inlet SO ₂ (%)	2.4-4.9	2.1-5.4

Table 3. Comparison of Bench-Scale and “6X” DSRP Slipstream Test Units

	1X “Bench-scale” (fixed-bed)	6X “Pilot” unit (fluidized-bed)
Flow rate (regeneration off-gas and coal gas) (std L/min [std ft ³ /h])	75 (170)	up to 330 (750)
SO ₂ concentration in regeneration off-gas (%)	2 to 5	up to 14
Catalyst volume	1 L	1.5 L
Space velocity (std cm ³ /cm ³ h)	5,000	up to 13,000
Sulfur production rate (g/h)	110	up to 2,200
Reactor I.D. (cm [in.])	7.6 (3.0)	12.7 (5.0)
Tubing O.D. (mm [in.])	9.5 (3/8)	19 (3/4)



Figure 2. 6X skid in RTI fabrication shop, gas inlet end.



Figure 3. 6X skid in RTI fabrication shop, gas outlet end.

Results

The following items highlight the key results of the DSRP development that has taken place, thus far, with the emphasis on actual coal gas testing:

- The 1995 slipstream test achieved more than 160 h of on-stream time and demonstrated that a single-stage process achieved consistent performance when the coal gas stoichiometry was carefully controlled.
- The conversion of 98 percent of the incoming sulfur compounds to elemental sulfur was achieved at both the beginning and end of the runs, showing no observable catalyst deactivation due to the trace contaminants of actual coal gas.
- The additional exposure to actual coal gas during the canister testing in 1996 resulted in a total of 360 h of exposure to a batch of DSRP catalyst.
- A conversion of 96 percent was achieved in laboratory bench-scale testing of the exposed catalyst.
- Carbon deposits on the exposed catalyst, caused by the unique conditions (tar particles in the GE gas) of the GE canister test, were believed to be the cause of an initial poor performance of the exposed catalyst; the carbon gradually vaporized from the catalyst as the bench-scale testing proceeded.

Applications/Benefits

The results of the development work conducted on this project show that, after a significant exposure time to actual coal gas, the DSRP catalyst continues to function in a highly efficient manner to convert SO_2 in a simulated regeneration off-gas to elemental sulfur. This demonstration of a rugged, single-stage catalytic process resulted in additional on-line experience and the assembling of more process engineering data. The development of the DSRP continues to look favorable as a feasible commercial process for the production of elemental sulfur from hot gas desulfurizer regeneration off-gas.

Future Activities

Active planning is under way for future activities on this contract. Canisters of fixed-bed DSRP catalyst have been prepared for another exposure test with actual coal gas, this time at FETC's Power Systems Development Facility (PSDF) at Wilsonville, Alabama. Exposure is expected to take place some time during FY 1998. The current research by others suggests that future commercial HGD processes—using undiluted air and fluidized-bed regenerators—are likely to produce higher concentrations of SO_2 in the regeneration off-gas than was the case at the start of the DSRP development. This trend suggests that the DSRP should also be tested in a fluidized-bed configuration to deal with the higher exothermicity associated with higher concentration streams. Additional development and testing of a fluidized-bed process is planned, capable of producing elemental sulfur from 14 percent SO_2 at HTHP. Two candidate fluidizable DSRP

catalysts have been prepared for testing, in cooperation with a catalyst manufacturer. The initial tests of one catalyst show promising results for sulfur recovery from high SO₂ streams.

Planning is also under way to conduct a long-duration field test using the skid-mounted six-fold larger (6X) DSRP with a slipstream of actual coal gas at PSDF. Modification of the 6X unit will be completed, consistent with specific site requirements. The mobile laboratory will be refitted at RTI as a control room for the 6X unit and will be moved along with the skid-mounted 6X unit to Wilsonville, Alabama, for the testing to be conducted in FY 1998. Figure 4 shows an artist's conception of how the mobile laboratory will be used in conjunction with the 6X unit at that field test site.

Acknowledgments

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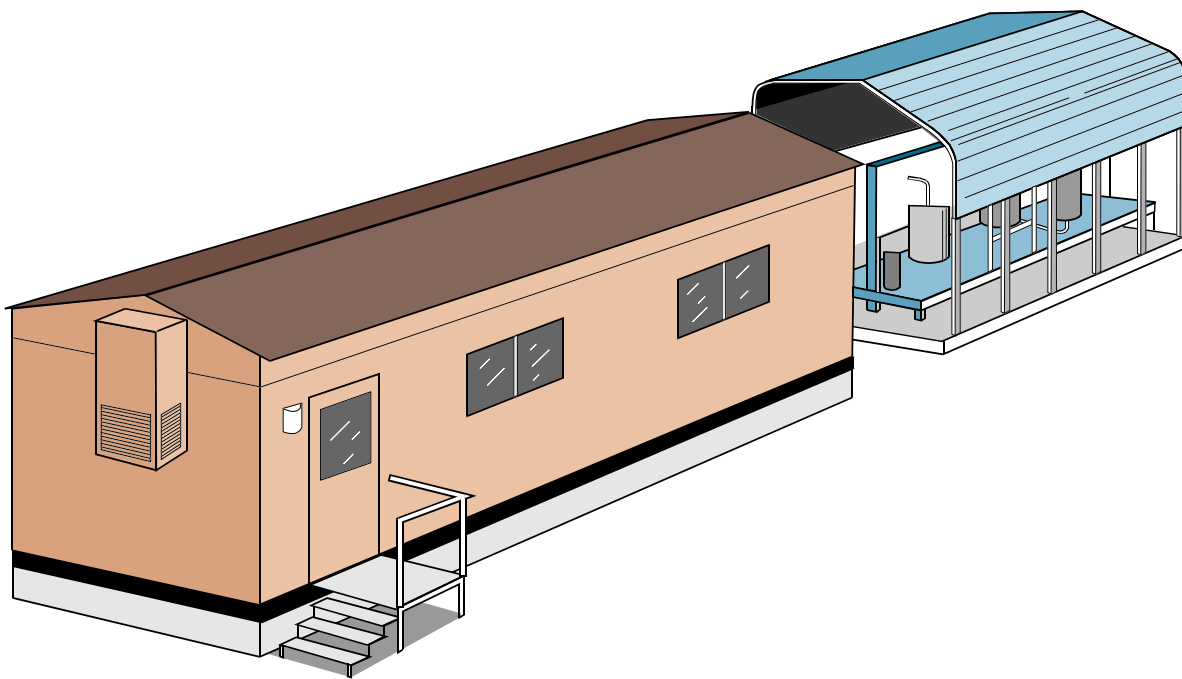


Figure 4. Mobile laboratory.

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